

Acoustical and Thermodynamical Study of Toluene in Cyclohexane & Nitrobenzene at 293K, 298K and 303K Using Ultrasonic Technique

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ABSTRACT

The ultrasonic studies in liquids are great use in understanding the nature and strength of molecular interaction. The thermo-acoustical parameters for ternary liquids mixtures namely, Toluene+ Cyclohexane + Nitrobenzene have been estimated, from the measured values of ultrasonic velocity (U), density (ρ) and viscosity (η). Using the measured data, some of the acoustical parameters such as, adiabatic compressibility (β_a) free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time (τ) and Gibb's free energy (ΔG) are evaluated at three different temperatures 293K, 298K and 303 K. The experimental density (ρ), viscosity (η) and ultrasonic velocity (U) have been measured for ternary mixtures containing Toluene+ Cyclohexane + Nitrobenzene at three different temperatures 293K, 298K and 303 K. The present paper represents the non- linear variation of ultrasonic velocity and the thermo-acoustical parameters lead to formation of donar – acceptor complex between toluene – nitrobenzene molecules and dipole – induced dipole interaction between nitrobenzene- cyclohexane molecules. The acoustical parameters such as adiabatic compressibility (β_a), free length (L_f)

and free volume (V_f), internal pressure (π_i), relaxation time (τ), acoustic impedance (Z) and Gibb's free energy (ΔG) have been calculated from experimental data. These parameters are used to discuss the molecular interactions in the liquid mixtures. The behavior of these parameters with composition of the mixture has been discussed in terms of molecular interaction between the components of the liquids.

Keywords: Ultrasonic velocity, acoustical parameters, molecular interaction, toluene, cyclohexane, nitrobenzene and ternary mixture.

1. INTRODUCTION

The ultrasonic study plays an important role in understanding the nature and strength of molecular interactions¹⁻⁵. Using intermolecular interaction we can understand the structural arrangement along with the shape of the organic molecules⁶⁻⁹. Regarding the molecular association in ternary mixtures having nitrobenzene as one of the components is of particular interest, since nitro group is highly polar and can associate with any other group having some degree of polar attractions¹⁰. Toluene is an aromatic compound, moderately polar due to hyper conjugation effect, associated through Vander Waal's force, mixed with nitrobenzene, the $-\text{NO}_2$ group which acts as an electron acceptor towards the π - electrons of toluene ring¹¹. This is due to the fact that $-\text{CH}_3$ group of toluene is an electron donor group through hyper conjugation, enhances the π - electron density of the toluene ring. Thus this makes the donation of π - electron for $-\text{NO}_2$ group easier forming donor – acceptor complex between toluene and nitrobenzene molecules and cyclohexane is a cyclic hydrocarbon, non- polar molecule, doesn't possess dipole moment, so there is

no association due to polarity but some extent there will be the existence of Vander Waal's force. In present study, the molecular interaction of toluene in cyclohexane and nitrobenzene has been characterized at different temperature 293K, 298K and 303K. The addition of nitrobenzene, which is non-associative and highly polar when added to non-polar toluene molecules, induces dipole moment and further addition of cyclohexane (non-polar) leads to new kind of dipole- induced dipole interaction for formation of complex between cyclohexane and toluene molecules.

2. MATERIALS AND METHODS

The liquid mixtures of various concentrations in mole fraction were prepared by taking AR grade chemicals. In the ternary mixture system, the mole fraction of second component, cyclohexane(X_2) is kept fixed arbitrarily at $X_2 = (0.40)$. Mole fraction of toluene (X_1) is increased from 0.00 to 0.60 while mole fraction of nitrobenzene (X_3) is decreased from 0.60 to 0.00. The ultrasonic velocity in the liquid mixtures have been measured using an ultrasonic interferometer (Mittal type:

Model: M-83) working at frequency 3 MHz with an overall accuracy of $\pm 0.1 \text{ ms}^{-1}$, an electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of a steel containing the experimental solution at the desired temperature. The density of pure liquids and liquid mixtures was determined using a 25ml specific gravity bottle with an accuracy of $\pm 0.1 \text{ Kg m}^{-3}$. An Ostwald's viscometer was used for the viscosity measurement of pure liquids and liquid mixtures with accuracy. The viscometer was calibrated before used. The time of flow of water (t_w) and time flow of solution (t_s) was measured with digital stop watch. All the precautions were taken to minimize the possible experimental error.

3. THEORY

- **Adiabatic compressibility (β_a)** has been calculated from the ultrasonic velocity (U) and the density (ρ) of the medium using the equation as:

$$\beta_a = 1 / U^2 \rho \quad (1)$$

- **Intermolecular free length** has been determined as:

$$L_f = K_T (\beta_a)^{1/2} \quad (2)$$

Where K_T – is a Jacobson's constant.

- **Free volume** in terms of ultrasonic velocity (U) and viscosity of the liquid (η) as :

$$V_f = [M_{\text{eff.}} U / K\eta]^{3/2} \quad (3)$$

Where, M_{eff} is the effective molecular weight ($M_{\text{eff.}} = \sum m_i X_i$, in which m_i and X_i are the molecular weights and the mole fraction of the individual constituents respectively). K is a temperature independent constant which is equal to 4.28×10^9 for all liquids.

- **Internal pressure** is calculated by

$$\Pi_i = bRT (K \eta / U)^{1/2} (\rho^{2/3} / M^{7/6}) \quad (4)$$

Where, b stands for cubic packing which is assumed to be 2 for all liquids and K is a dimension less constant, independent of temperature and the nature of liquids and its value is 4.28×10^9 , T is the absolute temperature and M_{eff} is the effective molecular weight.

- **Relaxation time** in terms of adiabatic compressibility (β_a) and viscosity of the liquid (η) as:

$$\tau = 4/3 \beta_a \eta \quad (5)$$

- **Gibb's free energy** can be calculated from the following relation:

$$\Delta G = KT \log (K\tau / h) \quad (6)$$

Where, τ is the relaxation time, K the Boltzmann constant, T the absolute temperature and h is the Planks constant.

Table (1):- The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) for the ternary system: - Toluene + Cyclohexane + Nitrobenzene at 293K, 298K and 303K.

Mole Fraction		Density (ρ) (Kg m^{-3})			Viscosity (η) ($10^{-3} \text{ N s m}^{-2}$)			Ultrasonic velocity (U) (ms^{-1})		
X_1	X_3	293K	298K	303K	293K	298K	303K	293K	298K	303K
0.0000	0.6000	1025.9	1024.1	1022.4	1.4800	1.2900	1.1400	1335.0	1320.0	1298.4
0.1000	0.5000	998.53	996.75	994.97	1.3000	1.1500	1.0190	1314.0	1302.0	1286.4
0.1999	0.4001	948.99	947.36	942.94	1.2100	1.0530	0.9110	1312.8	1291.2	1279.2
0.2999	0.3001	938.56	936.86	934.77	1.0710	0.9194	0.8131	1309.2	1282.2	1263.0
0.4000	0.2000	899.29	897.76	896.25	0.9520	0.8321	0.7241	1282.8	1260.0	1245.6
0.5001	0.0999	860.15	858.24	856.74	0.8040	0.7071	0.6245	1268.4	1251.6	1231.2
0.6000	0.0000	856.95	855.88	854.17	0.7220	0.6290	0.5550	1258.2	1248.0	1222.2

Table (2):- The experimental values of adiabatic compressibility (β_a), free length (L_f), and free volume (V_f), for the ternary system- Toluene + Cyclohexane + Nitrobenzene at 293K, 298K and 303K.

Mole Fraction		Compressibility (β_a) ($10^{-10} \text{ m}^2 \text{ N}^{-1}$)			Free length (L_f) (10^{-11} m)			Free volume (V_f) ($10^{-7} \text{ m}^3 \text{ mol}^{-1}$)		
X_1	X_3	293K	298K	303K	293K	298K	303K	293K	298K	303K
0.0000	0.6000	5.4689	5.6036	5.8016	4.5602	4.6870	4.8173	1.0778	1.3028	1.5661
0.1000	0.5000	5.8002	5.9181	6.0734	4.6963	4.8168	4.9288	1.2242	1.4560	1.7334
0.1999	0.4001	6.1141	6.3313	6.4809	4.8217	4.9821	5.0915	1.2939	1.5620	1.9490
0.2999	0.3001	6.2561	6.4925	6.7063	4.8617	5.0451	5.1793	1.4860	1.8190	2.2189
0.4000	0.2000	6.7573	7.0161	7.1913	5.0690	5.2446	5.3633	1.6380	1.9527	2.3646
0.5001	0.0999	7.2262	7.4380	7.6999	5.2419	5.3999	5.5497	1.9752	2.3753	2.7601
0.6000	0.0000	7.3712	7.5016	7.8373	5.2942	5.4230	5.5990	2.1766	2.6471	3.0955

Table (3):- The experimental values of internal pressure (π_i), relaxation time (τ), and Gibb's free energy (ΔG) for the ternary system- Toluene + Cyclohexane + Nitrobenzene at 293K, 298K and 303K.

Mole Fraction		Internal pressure (π_i) (10^6 Pa)			Relaxation time (τ) (10^{-12} s)			Gibb's free energy (ΔG) ($10^{-20} \text{ KJmol}^{-1}$)		
X_1	X_3	293K	298K	303K	298K	303K	308K	298K	303K	308K
0.0000	0.6000	460.54	439.21	422.23	1.0798	0.9641	0.8797	0.6378	0.6133	0.5957
0.1000	0.5000	442.04	423.83	406.12	1.0056	0.9057	0.8175	0.6121	0.5904	0.5684
0.1999	0.4001	427.99	408.34	386.73	0.9904	0.8897	0.7877	0.6066	0.5839	0.5545
0.2999	0.3001	414.15	393.88	378.90	0.8877	0.7959	0.7270	0.5672	0.5431	0.5246
0.4000	0.2000	398.08	381.40	363.43	0.8581	0.7784	0.6942	0.5550	0.5349	0.5074
0.5001	0.0999	371.17	354.47	342.43	0.7748	0.6959	0.6412	0.5182	0.4938	0.4778
0.6000	0.0000	366.75	349.16	336.53	0.7101	0.6291	0.5799	0.4867	0.4569	0.4404

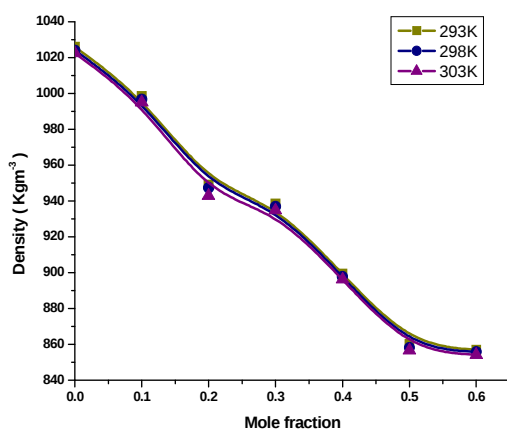


Fig.(1) Variation of density with mole fraction of toluene.

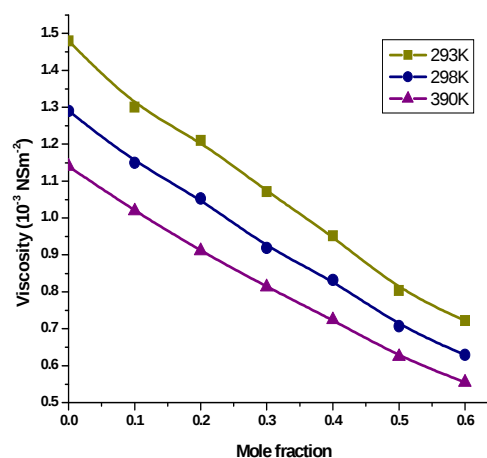


Fig.(2) Variation of viscosity with mole fraction of toluene.

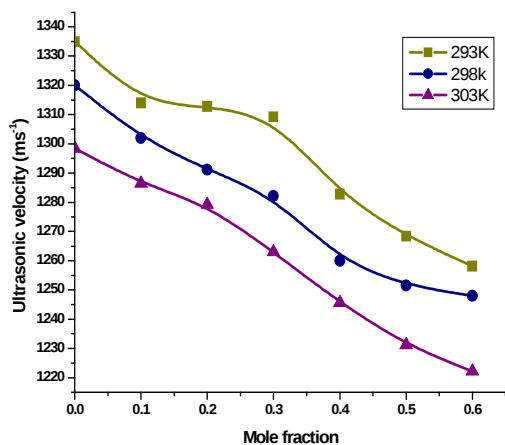


Fig.(3) Variation of ultrasonic velocity with mole fraction of toluene.

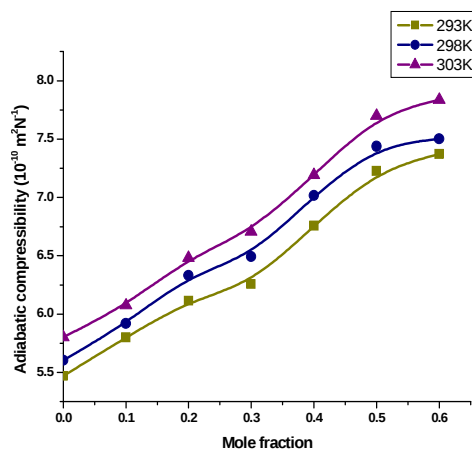


Fig.(4) Variation of adiabatic compressibility with mole fraction of toluene.

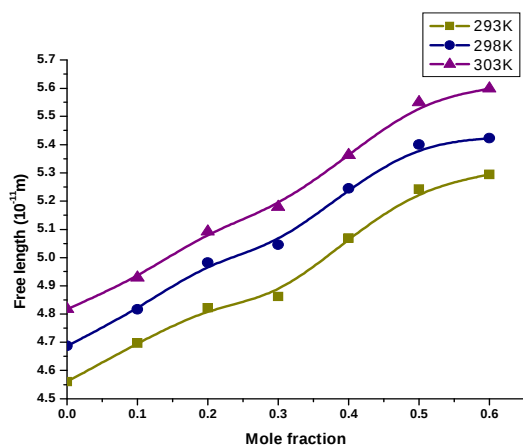


Fig.(5) Variation of free length with mole fraction of toluene.

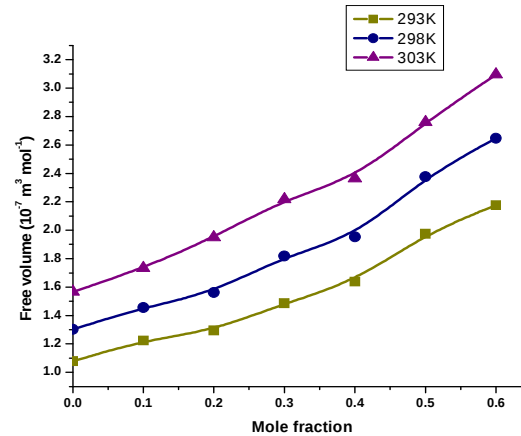


Fig.(6) Variation of free volume with mole fraction of toluene.

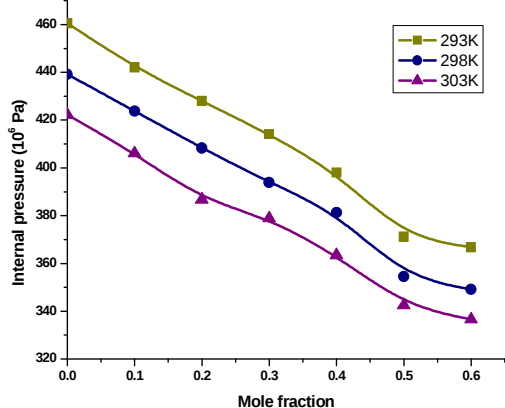


Fig.(7) Variation of internal pressure with mole fraction of toluene.

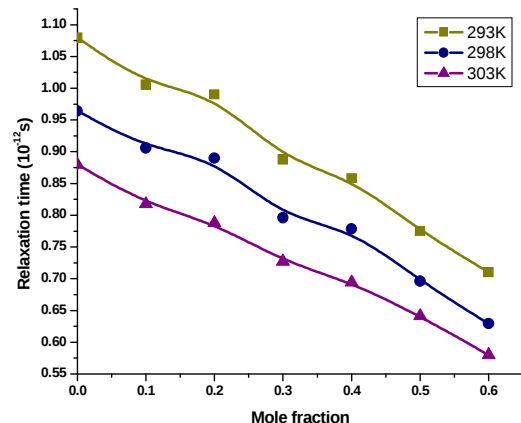


Fig.(8) Variation of relaxation time with mole fraction of toluene.

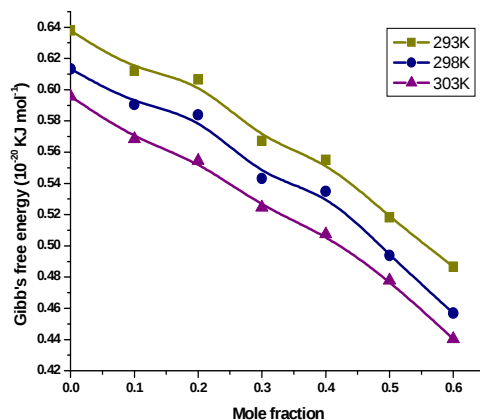


Fig.(9) Variation of Gibbs's free energy with mole fraction of toluene.

Graphs: Fig. 1-9, shows the variation of ultrasonic velocity (U), density (ρ), viscosity (η) adiabatic compressibility (β_a) free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time (τ) and Gibb's free energy (ΔG) with respect to mole fraction of toluene at different temperature 293K, 298K, 303K.

4. RESULTS AND DISCUSSIONS

The experimentally measured values of density (ρ), viscosity (η) and ultrasonic velocity (U), for the ternary system namely, Toluene + Cyclohexane + Nitrobenzene at different temperature 293K, 298K and 303K presented in **Table-1**. The acoustical parameters such as adiabatic compressibility (β_a), free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time (τ) and Gibb's free energy (ΔG) with respect to mole fraction of toluene at different temperature 293K, 298K, 303K are given in **Table-2** and 3.

From the **Table-1**, it is found that the ultrasonic velocity, density and viscosity decreases with increase in mole fraction of toluene for the ternary system. The variation of ultrasonic velocity in solution depends upon the increase or decrease of intermolecular free length after mixing the components, based on a model for sound propagation proposed by Eyring and

Kincaid¹². The decrease in velocity is perhaps due to structural changes occurring in the mixtures resulting in weakening of intermolecular forces¹³. Further the ultrasonic velocity (Fig.1) decreases with increase in temperature at any concentrations as rise in temperature leads to less disordered structure and more spacing between the molecules. The decrease in density (Fig.2) and viscosity (Fig.3) with temperature indicates that decrease in intermolecular forces due to increase in thermal energy of the system, which cause increase in volume expansion and hence increase in free length. It is found that from **Table-2**, the adiabatic compressibility, free length and free volume increases with increasing mole fraction of toluene for the ternary system. The adiabatic compressibility shows an inverse behavior as compared to ultrasonic velocity. This indicates that there is a significant interaction between nitrobenzene and toluene through dipole-induced dipole interaction.

From the **Table-3**, the reduction in internal pressure may be due to the loosening of cohesive forces and adhesive force leading to breaking the structure of the solution of nitrobenzene and cyclohexane. When the temperature is increased, there is a tendency for the mixture molecules to move away from each other, reducing the possibility for the interaction, which may further reduce the cohesive forces as well as adhesive force and ultimately leads to an increase in the free volume as shown in (Fig.7). Also we observed that in the absence of toluene molecule, there is stronger interaction between nitrobenzene and cyclohexane while in the absence of nitrobenzene molecule, the interaction between toluene and cyclohexane is weak. The relaxation time decreases with increase in mole fraction of toluene and increase in temperature as shown in (Fig.8). The relaxation time is in the order of 10^{-12} sec. is due to structural relaxation process¹⁴ showing the presence of molecular interaction. The reduction in Gibb's free energy (Fig.9) in the present ternary system indicates that the need for smaller time for the cooperative process or the rearrangement of molecules in the mixtures decreases the energy that leads to dissociation¹⁵.

5. CONCLUSION

It is concluded that ultrasonic studies provide a comprehensive investigation of molecular association between nitrobenzene and cyclohexane and molecular dissociation between toluene and cyclohexane. Also we observed that associative interaction between nitrobenzene and cyclohexane is decrease due to increase of mole fraction of toluene.

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